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(54) MATERIAL FOR LITHIUM ION SECONDARY BATTERY, ITS PRODUCTION AND BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a boron-substituted graphite having a flat discharge potential, excellent in cycle characteristics and having a low ratio of boron bonded to nitrogen by carbonizing an infusibilized carbonaceous material containing a boron compound mixed and added thereto, then rapidly carrying out the temperature increase in an inert atmosphere unreactive with boron, conducting a graphitizing treatment and subsequently quenching the resultant treated material.

SOLUTION: The amount of an added boron compound (e.g. boric acid or boron oxide) based on a raw material pitch is preferably 0.1-7 wt.% based on the pitch having a high softening

point and expressed in terms of boron element. A liquid pitch used is preferably a fraction remaining after carrying out a vacuum distillation of a coal tar obtained by removing a light portion according to an atmospheric distillation and has preferably 100-115°C softening point. The carbonaceous material containing the boron compound added thereto is finely pulverized to provide a particle diameter of 200-mesh undersize and the resultant pulverized material is then subjected to an oxidizing treatment at 140-300°C in air and finally subjected to a carbonizing treatment at 600-1,200°C. No problem is caused if the atmosphere at the time of carbonizing is either a reducing gas or nitrogen which is an inert atmosphere without oxidizing carbon.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention aims at offer of a carbonaceous ingredient highly efficient as a negative-electrode ingredient for rechargeable lithium-ion batteries etc.

[0002]

[Description of the Prior Art] In recent years, a miniaturization and lightweight-izing of electronic equipment or communication equipment are progressing quickly, and the rechargeable lithium-ion battery which the demand of a miniaturization and lightweight-izing is strong, and is a high energy consistency, and has a high voltage also to the rechargeable battery used as these power sources for a drive is proposed. A rechargeable lithium-ion battery uses for example, a cobalt acid lithium for a positive electrode, uses carbonaceous ingredients, such as a graphite, for a negative electrode, carries out occlusion of the lithium ion to a negative electrode at the time of charge, and makes these lithium ions emit from a negative electrode at the time of discharge.

[0003] although what carbonized or graphitized the carbonaceous raw material or resin like a particle of MCMB (meso carbon micro bead) or a mesophase pitch guide from petroleum or the heavy oil of a coal system as this negative electrode ingredient be use , as a cell , a high discharge capacity be obtain and its initial effectiveness be necessarily so high , either .

[0004] In order to solve these troubles, the carbonaceous ingredient which added boron is examined variously. J.R.Dahn and others (7 45 Phys.Rev.B.Vol. No. 3773 (1992)) will add about 8% of the weight of boron oxide by boron conversion to an artificial graphite in 1992. Although the boron permutation graphite graphitized under nitrogen-gas-atmosphere mind is examined as host material of INTAKARENTO of a lithium, in this reference, the property as actual cells, such as discharge capacity and initial effectiveness, is not described.

[0005] Moreover, instead of the contents given in JP,5-266880,A adding boron to an artificial graphite like the above-mentioned reference, in the organic substance which is a raw material, it only added, boron was only graphitized, and the contents of the above-mentioned official report are not different from the contents of said reference at all.

[0006] Moreover, in JP,8-31422,A, JP,9-63584,A, etc., although the raw material of the graphite which should be manufactured is limited to a pitch, or graphitization temperature is limited in order to prevent increase of graphite particle diameter, only on condition that this, the carbonaceous ingredient optimal as a negative-electrode ingredient for lithium ion batteries is not obtained. Furthermore, although it has pointed out causing the fall of the discharge capacity in JP,8-31422,A when the boron carbide which remains in the carbonaceous ingredient obtained uses as a negative electrode of a cell, it is only controlling the amount of the boron compound added as the solution, and, similarly the carbonaceous ingredient optimal as a negative-electrode ingredient for lithium ion batteries is not obtained.

[0007] Moreover, by JP,10-162829,A, in order to consider industrial manufacture of these boron permutation graphite, after graphitizing a carbonaceous ingredient under nitrogen-gas-atmosphere mind, it is indicating making it decrease by carrying out reduced pressure processing for the boron nitride

generated to a surface layer above 2000 degrees C, or carrying out halogen processing.

[0008] However, the equipment to be used becomes complicated and performing such processing requires cost, in order to manufacture a negative-electrode ingredient industrially. Therefore, although distributing a boron compound in the pitch which carried out softening fusion is indicated in JP,10-255799,A in order to avoid nitrogen-gas-atmosphere hindrance and contact of a boron compound, it is very difficult to wrap a boron compound in a pitch completely, and it has a question about the effectiveness. In addition to the above-mentioned official report, there is nothing that touched on the controlled atmosphere at the time of graphitizing a carbonaceous ingredient not much, and it is described that the most graphitizes "under an inert atmosphere" to a carbonaceous ingredient.

[0009] Boron is indicated in JP,3-245458,A to these boron permutation graphites about the carbonaceous ingredient which added a permutation or boron. However, only processing to carbonization is carried out but the carbonaceous ingredient currently indicated in this official report completely differs from the boron permutation graphite which permuted some carbon of the graphite described previously by boron.

[0010] Moreover, JP,7-73898,A is indicating the carbonaceous ingredient which permuted some carbon atoms of graphite or amorphous graphite by boron. However, when this carbonaceous ingredient also uses that the distance between graphite layers by the X diffraction (d002) is 0.337nm or more, and this as a negative-electrode ingredient of a cell, the charge-and-discharge curve as a cell of the boron permutation graphite by which the thing of graphite permuted some carbon of the graphite which the point described from differing by boron is a greatly different ingredient.

[0011] Moreover, when it is compounded by the CVD method which used the mixed gas of the source gas of boron, and carbon source gas and industrial manufacture is considered so that the carbonaceous ingredient which permuted or added boron by these boron may be looked at by JP,7-73898,A, JP,6-333601,A, etc., these approaches are impractical in cost.

[0012] Many things are examined also about the carbon material which added silicon in addition to the carbonaceous ingredient which added these boron. Alloying with a lithium atom is known and silicon becomes 4017 mAh/g extent as an amount of specific volume. However, irreversible capacity is large and a problem is in the stability for the cubical expansion accompanying alloying.

[0013] In order to solve this problem, the matter built into the quality of graphitized carbon which is a host substance in JP,7-315822,A, without changing the structure of the field which was ready in the host substance in the atom of the element which makes a lithium and alloys, such as silicon, is proposed. However, since it is necessary to perform expensive synthetic approaches, such as a CVD method, and in order to manufacture these matter, and silicon is inserted between carbon on atomic level, it is not improved about a big irreversible capacity.

[0014] Although the carbonaceous ingredient with which boron and silicon are intermingled is indicated by WO 98/24134, JP,11-40158,A, etc., boron and silicon are added into a carbonaceous ingredient, these matter is graphitized and its improvement of discharge capacity is not large.

[0015]

[Problem(s) to be Solved by the Invention] Therefore, discharge potential of this invention is flat as an object for rechargeable lithium-ion batteries, it is excellent in a cycle property, and aims at offering industrially the boron permutation graphite of high capacity, and a silicon content carbonaceous ingredient by high density rather than the conventional carbonaceous ingredient.

[0016]

[Means for Solving the Problem] The above-mentioned purpose is attained by the following this inventions. That is, after this invention performs a temperature up promptly and carries out graphitization processing in boron and the inert atmosphere which does not react after carbonize the non-deliquesce carbonaceous ingredient which carried out mixed addition of the boron compound, by the manufacture approach characterize by quench, there are few rates of the boron combined with nitrogen, it is high-density, and offers the boron permutation graphite which is the lithium ion battery ingredient of high capacity. Moreover, the silicon content carbonaceous [which it is high-density and is the lithium ion battery ingredient of high capacity] ingredient manufactured by adding and heat-treating

silicon to high crystal graphites, such as carbide of a carbonaceous ingredient, a graphitization object, or a natural graphite, and the boron permutation graphite further mentioned above is offered.

[0017] this invention persons invented the manufacture approach of a boron permutation graphite of having the cell property which was excellent also in the boron permutation graphite, and the boron permutation graphite manufactured by the manufacture approach. Moreover, the silicon content carbonaceous [which it is high-density and is the lithium ion battery ingredient of high capacity] ingredient manufactured by adding and heat-treating silicon to high crystal graphites, such as a graphitization object of a carbonaceous ingredient or a natural graphite, and the boron permutation graphite further mentioned above, and its manufacture approach were invented. Although theoretical consideration about this invention is performed below, this invention is not restricted at all by the justice of these considerations.

[0018] That is, as a general method of obtaining a boron permutation graphite, as C.E.Lowell (Journal of The American Ceramic Society Vol.50, No.3,142 (1967)) has proposed, it is an approach with the easiest approach of graphitizing a carbonaceous ingredient for the bottom of existence of a boron compound. Under the present circumstances, in order to permute some carbon atoms of a carbonaceous ingredient by homogeneity by boron, it is important to mix a boron compound with a carbonaceous ingredient to homogeneity. For that purpose, particle size of the boron compound to mix can be made small, or the approach of making it liquefied, adding and processing a boron compound can be considered. The concrete approach of mixing a boron compound to homogeneity at a carbonaceous ingredient is later described in a detail.

[0019] What kind of gestalten, such as inorganic boron compounds, organic boron compounds, etc., such as boric acid, boron oxide, boron carbide, and a boron element, are sufficient as the boron compound added into a carbonaceous ingredient. However, about a carbonaceous ingredient, the wettability to the boron compound added is good, it is easy to build the carbide of boron, and what is the ingredient of graphitizability is the optimal. Permutation dissolution of the carbon by boron is the following, and the reason such a carbonaceous ingredient is required is that it is thought that it is for making and progressing.

[0020] If the mixture of a carbonaceous ingredient and a boron compound is heated regardless of the gestalt of the added boron compound in boron and the ambient atmosphere which does not react and temperature is raised, first, both will act and boron carbide will generate. The generation reaction rate of the boron carbide at this time changes with the qualities of the carbonaceous ingredient used as a raw material a lot. Therefore, about the carbonaceous ingredient to be used, wettability is good to a boron compound and what is easy to build the carbide of boron is good. In the interface of this generated boron carbide, it has the field which can do the solid solution of the carbon and boron which are indicated to be B_4C_{1-x} , and boron carries out dissolution diffusion during the carbon organization from this part. It becomes the boron permutation graphite from which distortion of the crystal of the graphite to generate was removed, consequently graphite structure developed by this dissolution diffusion.

[0021] In order for the above-mentioned graphite structure to progress, it is good that the carbonaceous ingredient used as a raw material is an ingredient of *****. this invention persons had the quick generation rate of boron carbide, and as a result of examining wholeheartedly the coal-for-coke-making genius ingredient used as graphitizability, they found out that the high softening temperature pitch containing an optical-isotropy part was the optimal.

[0022] Moreover, in order for graphitization to advance by permutation dissolution of the carbon by the above boron and to manufacture a uniform boron permutation graphite, the controlled atmosphere at the time of graphitizing is important in the first place. On the other hand, in JP,10-162829,A, although it has proposed graphitizing by nitrogen-gas-atmosphere mind from a viewpoint of cost consequently, a boron compound and the nitrogen of an ambient atmosphere react, boron nitride generates, and when only existence of this boron nitride uses the graphite obtained as a negative-electrode ingredient of a cell, the purport which is the cause which lowers that cell property is indicated.

[0023] However, only existence of the boron nitride which this invention persons generated found out that it was the cause which serves as a failure at the time of the boron which the generation reaction of

this boron nitride under graphitization instead of a problem described previously carrying out dissolution diffusion during a carbon organization, and a boron permutation graphite with the uniform generation reaction of the above-mentioned boron nitride does not generate. Therefore, graphitization temperature at the time of graphitizing a carbonaceous ingredient was made into 2200 degrees C or more, and it found out that it was necessary to use it as a controlled atmosphere at the time of graphitizing an inert atmosphere which does not cause a reaction with boron during a graphitization reaction, for example, an argon, helium or the argon that contained nitrogen in extent which is not nitrated, helium, etc.

[0024] Although it changes with the format of equipment, the additions of a boron compound, etc. about the heating up time to the temperature which a carbonaceous ingredient graphitizes, graphitization temperature, its holding time, and the cooldown delay after graphitization, a temperature up is carried out to the temperature which generally graphitizes a coal-for-coke-making genius ingredient within [in 100 hours], graphitization temperature is made into 2200 degrees C or more, and the holding time is made into 48 [zero -]:00. Although the boron carbide of initial addition during this graphitization or the boron carbide to generate causes increase of graphite particle diameter by fusing if it becomes 2400 degrees C or more, in order to prevent this, a high crystal graphite with effectiveness which makes low bulk density at the time of graphitization a little is added. Then, a desirable result is obtained by cooling within [in 100 hours] from graphitization temperature to 100 degrees C.

[0025] The boron which dissolved to carbonaceous is very important for the cooling rate in this case on the front face of a generation graphite in the semantics of lessening the amount which re-deposits as B₄C and making particle size of B₄C which re-deposited small. It is because B₄C in a graphite does not contribute to the reversible occlusion of a lithium ion, but irreversible capacity is made to increase further or the conductivity of a graphite is checked, when a graphite is used as a negative-electrode ingredient of a rechargeable lithium-ion battery.

[0026] XPS can estimate the amount of B₄C which deposited on this graphite front face. As a negative-electrode ingredient for rechargeable lithium-ion batteries B₁s peak resulting from the permutation dissolution boron near 186eV exists in 1s spectrum of boron. And it is necessary to carry out to below pentatomic % in the surface layer element of the boron obtained from the intensity ratio of B₁s peak resulting from the boron of B₄C near 188eV comparatively detected by XPS, and this condition is fulfilled by controlling the above-mentioned cooldown delay.

[0027] About a silicon content carbonaceous ingredient, to a high crystal graphite or boron permutation graphites, such as a graphitization object of a carbonaceous ingredient, and a natural graphite, silicon or a silicon compound is added and it is manufactured by heat-treating at 350-1500 degrees C in an inert atmosphere and a reducing atmosphere, or a fine oxidizing atmosphere. Although it is thought that the compound by carbon, silicon, boron, and oxygen generates, it is the low irreversible capacity which is not considered only with the single crystal of silicon, and a big discharge capacity is shown by this heat treatment, it is not clear for details.

[0028]

[Embodiment of the Invention] Next, the gestalt of desirable operation is explained in order of the production process of a boron permutation graphite. Moreover, the manufacture approach of a silicon content carbonaceous ingredient is also explained.

[0029] (Addition of a boron compound) In this invention, in case a boron compound is added into the carbonaceous ingredient of a raw material, it is desirable to use that which the high softening temperature pitch which shows the graphitizability which 5-98 capacity % Contained the strong optical-isotropy part of reducing power for the boron compound to this boron compound was distributed to homogeneity, and atomized this as a raw material of graphitization.

[0030] The following actuation is performed in order to manufacture the particle of the above-mentioned boron compound content pitch. A liquefied pitch is made to distribute a boron compound, it heat-treats, and five to 98 capacity % and the softening temperature 10-95 capacity % Included preferably make the strong optical-isotropy part of reducing power the high softening temperature pitch of 250 degrees C or more to a boron compound. About the boron compound distributed in this pitch, although a liquefied ingredient is sufficient, in the case of a solid material, in order that the direction of the thin liner of

particle size may distribute to homogeneity, it is desirable, for example, it is desirable that mean particle diameter uses a particle 50 micrometers or less.

[0031] To the high softening temperature pitch which heat-treated and was generated, by boron element conversion, 0.1 % of the weight to 7% of the weight, the addition of the boron compound to a raw material pitch is added so that it may become 1 - 5% of the weight of a rate preferably. In the addition which is less than 0.1 % of the weight, a boron compound volatilizes between graphitization processings and a boron permutation graphite does not fully generate. On the other hand, it is not suitable in order to reduce the cell property of a graphite that B4C which does not dissolve in the graphite to generate when an addition exceeds 7 % of the weight generates superfluously, and this B4C is obtained.

[0032] The liquefied pitch used above is the fraction which carried out vacuum distillation of the coal tar except a light part further, and remained with atmospheric distillation, and that [its] the softening temperature of whose is 100-115 degrees C is desirable. There is much matter pyrolyzed in case softening temperature heat-treats in the pitch of less than 100 degrees C after adding a boron compound, and un-arranging, such as taking heat treatment time amount for a long time, arises. Moreover, when the liquefied softening point of pitch exceeds 115 degrees C, the viscosity of the heat treatment first stage after boron compound addition is high, and distribution of the added boron compound is not desirable at the reason of fully being unable to carry out within heat treatment time amount.

[0033] About heat treatment at the time of particle manufacture of the above-mentioned boron compound content pitch, 420 degrees C or less are preferably heat-treated at 380-400 degrees C. In the meantime, **** by blowing in of nitrogen gas is performed through two or more nozzles from mechanical **** and the reactor pars basilaris ossis occipitalis of a melting pitch, the homogeneity of the temperature of a melting pitch is maintained, and the maldistribution of a pitch component is prevented, and the dispersibility of a boron compound is secured.

[0034] As for the above heat treatment, it is desirable to carry out by the softening temperature of a heat treatment object setting up conditions, such as heating time and a pressure, whenever [stoving temperature] so that 250 degrees C or more may become the range of 330-370 degrees C preferably. A particle carries out softening fusion in the case of oxidation treatment whose softening temperature of a heat treatment object is degree process after pulverizing of a heat treatment object at less than 250 degrees C, and a configuration cannot be held. It is not desirable in respect of on the other hand, the aspect ratio of the particle obtained by grinding which handling of the extract of the heat treatment object from the container after heat treatment etc. becomes difficult, or is degree process becoming large, if the softening temperature of a heat treatment object exceeds 370 degrees C etc.

[0035] The high softening temperature pitch which shows the graphitizability which 5-98 capacity % Contained the strong optical-isotropy part of reducing power to the boron compound is generable by adding a boron compound to a raw material pitch as mentioned above. This is for the viscosity of the mixture under heat treatment rising and checking coalesce of the mesophase phase which is optical anisotropic texture by adding a boron compound.

[0036] To the added boron compound, wettability is good, and tends to build the carbide of boron, and the generation rate of a boron permutation graphite of the isotropic optical part of such a high softening temperature pitch is also quick. When such an optical-isotropy part is smaller than 5 capacity %, the generation rate of the boron permutation graphite of such overalls becomes slow. Moreover, when an isotropic optical part is larger than 98 capacity %, it becomes what was inferior in respect of graphitization nature.

[0037] Furthermore, in another desirable operation gestalt of this invention, a boron compound is made to adhere to a high crystallinity graphite (the shape of a scale), for example, the natural graphite of a minute particle size, or an artificial graphite at homogeneity, and the high softening temperature pitch which contained the optical-isotropy part for this 5 to 98% can be mixed. By doing in this way, homogeneity can be made to distribute the boron compound to the inside of a pitch further, and graphitization of the carbonaceous ingredient whose high crystal graphite is a raw material is promoted.

[0038] In order to make a boron compound adhere to a high crystallinity graphite at homogeneity For example, in the solution which dissolved boron compounds, such as boric acid and boron oxide, in the

solvent in which wettability is shown to a graphite like ethanol, or a liquefied organic boron compound Homogeneity distribution of the particle of a high crystal graphite can be carried out, organic substances, such as a solvent, can be removed by actuation of reduced pressure drying or a pyrolysis after that, and a boron compound can obtain to homogeneity the particle of the high crystal graphite which carried out distributed adhesion. As for the operating rate of the high crystal graphite in this case, and a boron compound, it is desirable in both sum total weight that a boron compound is 0.1 - 70% of the weight of a rate as boron.

[0039] Thus, when an optical-isotropy part mixes the mixture of the high crystal graphite and boron compound which are obtained in the high softening temperature pitch of 5 capacity % - 98 capacity %, the amount of mixing is 1 - 5 % of the weight preferably in boron element conversion to a high softening temperature pitch 0.1 % of the weight to 7% of the weight like the aforementioned case. A boron compound may add to homogeneity mixing with the high crystal graphite and high softening temperature pitch which carried out distributed adhesion at the time of heat treatment of a raw material pitch, or may carry out heat kneading of both by a kneader etc., or both may be mixed by particles using a ball mill etc.

[0040] (Atomization) The coal-for-coke-making genius ingredient with which the above boron compounds were added next is pulverized, and let the particle diameter be a 200-mesh undershirt. As mean particle diameter, 50 micrometers or less are preferably ground in the range of 5-30 micrometers. It is not limited especially as a grinder, for example, grinders, such as a jet mill, a ball mill, an agitation mill, and a high-speed tumbling mill, can be used.

[0041] (Non-deliqesce processing) Next, the above-mentioned particle is oxidized. This actuation is required in order for particles not to weld in the case of following carbonization and graphitization. Although this oxidation treatment may be performed at the temperature of 140-300 degrees C in air, it is desirable to pass nitrogen gas and to carry out all over an oxidation furnace, at 16 % of the weight - about 18 % of the weight of oxygen densities. Moreover, it is desirable that carry out hyperfractionation of the oxidation furnace, and, and process with the fluid bed or a particle performs passage in an oxidation furnace by the film so that a particle may not contact a heat source so that a particle may weld and an aggregate may not be formed on the occasion of oxidation. [that it can be made to do temperature control correctly] Although a certain amount of welding aggregate occurs by oxidation treatment, if choke crushing is carried out, the reuse of this welding aggregate can be carried out.

[0042] As for extent of oxidation, in this oxidation treatment, it is desirable to set up oxidation conditions so that an oxidation-treatment object may be in the condition that the oxygen which is about 2 % of the weight - about 10 % of the weight is included. It is inadequate in respect of a particle producing welding in a carbonization process as it is inadequate, under the above-mentioned range, i.e., oxidation, of the amount of oxygen, etc., and is not desirable in respect of the specific surface area of a particle becoming large on the other hand, if oxidation becomes superfluous, or the amorphous nature of a particle increasing etc.

[0043] Although it is lost although the reason of the particle which received the above oxidation treatment is unknown, and it is roundish and it cannot say that it is spherical, it became roundish [wore a little] and the aspect ratio is settled in the range of 1-2. [of an acute angle particle / before oxidation treatment / angle]

[0044] (Carbonization) Finally according to a conventional method, carbonization processing is performed. Carbonization processing is performed at 600 degrees C - 1200 degrees C. However, about the processing time, the optimal time amount is chosen with equipment. Moreover, if reducibility gas or nitrogen is also the inert atmosphere which does not oxidize carbon, even if it will use any, it is satisfactory. [of the ambient atmosphere at the time of carbonization] Also continuously these carbonization processings can be performed and various, conventionally well-known conditions and equipment can use it as it is as the various conditions and equipment of carbonization.

[0045] (Welding prevention) About the welding prevention at the time of graphitization, it carries out by the following approaches if needed. To the carbonaceous ingredient which was mentioned above and which carried out non-deliqesce processing, or the carbonaceous ingredient after carbonizing, the

impalpable powder of a high crystal graphite is added and mixed so that it may become 0.5 - 30% of the weight of the amount of the whole mixture. As for the impalpable powder of these quantities crystal graphite, it is desirable to use that whose mean particle diameter is 0.1-10 micrometers. Since what has mean particle diameter smaller than 0.1 micrometers needs special grinding, the effectiveness of welding prevention of a bigger thing than 10 micrometers is lost economically. About mixing, it is mixable with the conventional method of V blender, a Henschel mixer, etc.

[0046] (Graphitization) Graphitization for manufacturing the boron permutation graphite optimal as a negative-electrode ingredient for rechargeable lithium-ion batteries is performed by cooling within [in 100 hours] from the graphitization temperature to 100 degrees C, after carrying out the temperature up of the coal-for-coke-making genius ingredient to boron within [in 100 hours] under the inert atmosphere which does not react and graphitizing above 2200 degrees C. It is gas containing boron and the nitrogen of extent which does not cause nitriding of boron in rare gas, such as helium and an argon, or those gas as inert gas which does not react. These gas and the boron compound which reacted not only remain in the boron permutation graphite finally obtained, but in except for these boron and the gas which does not react, it will be prevented to dissolution diffusion into the graphite of boron.

[0047] Moreover, about graphitization temperature, it is known that graphitization nature will improve and 2200 degrees C or more with the quick rate boron carries out [a rate] dissolution diffusion all over a carbon organization are usually so suitable that it is high. Moreover, about the holding time of graphitization, it is 1 - 12 hours preferably for 0 to 48 hours. If the holding time of this temperature is too short like 0 hour, graphitization nature is late, and if it seems that it exceeds 48 hours, it happens and is not appropriate [the volatilization of boron which carried out dissolution diffusion the added boron and once]. Volatilization of a boron compound, the carbonization reaction of a boron compound, dissolution diffusion into the graphite of boron, etc. have taken place into this graphitization time amount.

[0048] Moreover, in order to manufacture the boron permutation graphite optimal as a negative-electrode ingredient for rechargeable lithium-ion batteries, the cooling rate from graphitization temperature to 100 degrees C is important. If a cooling rate is made quick, the amount to which the boron which dissolved re-deposits on a graphite front face as B₄C decreases, and particle size of B₄C which re-deposited can be made small. When it cools exceeding 100 hours to the temperature of 100 degrees C, there are many amounts of deposits of B₄C, and since the particle size also becomes large and causes increase of the irreversible capacity as a rechargeable lithium-ion battery negative-electrode ingredient etc., it is not desirable.

[0049] As current and a industrial graphitizing furnace, although the Atchison furnace type is mainly used, at this type of furnace, control of an ambient atmosphere, a cooling rate, etc. is also difficult, and it is unsuitable for manufacturing a boron permutation graphite with a sufficient cell property. In order to fulfill the above conditions, the graphite crucible in which the particle was inserted is continuously inserted in a graphitizing furnace, and a continuation graphitizing furnace which is cooled, or the kiln type and shaft kiln type continuation graphitizing furnace which can insert in fine particles continuously is the optimal. However, as long as it can keep the conditions of the above graphitization, you may not be such a furnace format.

[0050] (Many physical-properties values of a boron permutation graphite) For the distance between graphite layers (d₀₀₂), the magnitude (L_c) of the microcrystal of 0.337nm or less and the direction of a c-axis is [the magnitude (L_a) of the microcrystal of 30nm or more and the direction of an a-axis of the boron permutation graphite of this invention which were obtained by carrying out] a high crystal boron permutation graphite particle 40nm or more like the above. Moreover, it is below pentatomic % in the surface layer element of the boron obtained from the intensity ratio of B_{1s} peak which B_{1s} peak resulting from the permutation dissolution boron near 186eV exists in 1s spectrum of boron measured by XPS, and originates in the boron of B₄C near 188eV comparatively detected by XPS. Preferably, if the whole boron permutation graphite is 0.5 - 3 % of the weight still more preferably 0.01 % of the weight to 5% of the weight and the abundance as boron in a boron permutation graphite also uses the specific surface area of the particle as a negative-electrode ingredient for rechargeable lithium-ion batteries small

therefore below 2.0m²/g, a cell also with a comparatively small irreversible capacity also with low reactivity with the electrolytic solution will be obtained.

[0051] (measurement of XPS) Measurement of XPS is performed as follows. It fixes to the sample electrode holder for XPS analysis, without touching graphite powder empty-handed. The crevice of an electrode holder may be filled up with the approach of immobilization, and it may be lightly stuck to soft metals, such as an indium, by pressure. Next, it measures by introducing an electrode holder into a chemical laboratory. The processings on the front face of a sample (washing, ion sputtering, etc. of an organic solvent etc.) must not go before measurement. Measurement is performed according to the usual XPS measurement procedure (see the "X-ray photoelectron spectroscopy" (Maruzen, 1998) etc.). There is especially no limitation in X line light source. Binding energy is proofread using a standard sample. In this invention, gold is used for a standard sample and the binding energy of 4f 7 of golden / 2 peak is doubled with 84.0eV. The error of the binding energy in one equipment is less than +0.05eV. It is thought that they fit in the range of about +0.5eV dispersion although the criteria of binding energy change a little also with equipment manufacturers. Therefore, it is easy to distinguish three conditions, i.e., the dissolution boron, the boron carbide, and the boron nitride of boron by 1s spectrum of boron.

[0052] On the other hand, count of the elementary composition of a surface layer calculates first the integrated intensity of the peak which appears in 1s spectrum of boron. Although a peak may become unsymmetrical, it also takes into consideration and calculates asymmetry in this case. The method of asking for the integrated intensity of the peak of boron specifies the peak of the component of dissolution boron, boron carbide, and boron nitride with a Gaussian mold function, a Lorentz function, etc., and although the approach of fitting [a measured spectrum] is common, it does not adhere to this. The relative sensibility factor which accompanied calculating the presentation of a surface layer from the integrated intensity of a peak at equipment is used. In this invention, it calculated using carbon 1s:1.00, boron 1s:0.486, nitrogen 1s:1.80, and oxygen 1s:2.93. When the special element except having stated to the graphite here is not added, it is enough just to perform quantum count about these four elements. When a part of graphite particle is covered with other elements and compounds, the thickness of the covered layer etc. should be taken into consideration.

[0053] (Silicon content carbonaceous ingredient) About a silicon content carbonaceous ingredient, to a high crystal graphite or boron permutation graphites, such as a graphitization object of a carbonaceous ingredient, and a natural graphite, silicon or a silicon compound is added so that it may become 0.1 - 30% of the weight of the amount of the whole mixture by silicon conversion, and it is manufactured by heat-treating at 350-1500 degrees C in an inert atmosphere and a reducing atmosphere, or a fine oxidizing atmosphere. There is the following about the carbonaceous ingredient used as this base material. Carbonaceous ingredients, such as high crystal graphites, such as a thing which carbonized the pitch of thermosetting resin, such as phenol resin and furan resin, a coal system, and a petroleum system or a graphitized thing, a natural graphite and the decomposition graphite at the time of SiC manufacture, and kish graphite, and a boron permutation graphite of the invention concerned, can be mentioned.

[0054] Moreover, about the silicon or the silicon compound to add, single crystal silicon, polycrystalline silicon, an amorphous silicon, oxidation silicon, etc. are mentioned. About mixing of these carbonaceous ingredient, silicon, or a silicon compound, it is mixable with the conventional method of V blender, a Henschel mixer, etc. The silicon or the silicon compound to add is made into 0.1 - 30% of the weight of the amount of the whole mixture by silicon conversion. If an addition is made fewer than 0.1 % of the weight, the addition effectiveness of silicon will not appear. Moreover, if an addition is made [more] than 30 % of the weight, irreversible capacity will serve as a very big object.

[0055] (Application to a cell) The application to the rechargeable lithium-ion battery of the boron permutation graphite of this invention and a silicon content carbonaceous ingredient is explained below. The active material which forms an electrode plate is formed from the electrode coating liquid which consists of an active material and a binder (binder) at least. A rechargeable lithium-ion battery with a high discharge voltage of about 4 volts is obtained by using the boron permutation graphite of said this invention, or a silicon content carbonaceous ingredient as a negative-electrode active material, and using as positive-electrode matter combining kinds of the chalcogen compounds, such as lithium oxides, such

as LiCoO_2 and LiMn_2O_4 , TiS_2 , MnO_2 and MoO_3 , and V_2O_5 , or two or more of these sorts, for example. As for these active materials, it is desirable that homogeneity distributes in the coating film formed. For this reason, it is desirable that the mean particle diameter which has the particle size of the range of 1-100 micrometers as a forward and negative active material uses still more preferably about 5-40 micrometers of about 10-25-micrometer particles.

[0056] Moreover, as a binder of an active material layer, it can be used from thermoplastics, i.e., polyester resin, polyamide resin, polyacrylic ester resin, polycarbonate resin, polyurethane resin, cellulosic resin, polyolefin resin, polyvinyl resin, fluorine system resin, polyimide resin, etc., for example, being able to choose it as arbitration.

[0057] The active material layer which constitutes an electrode plate is created by the following approaches. First, the binder suitably chosen from the above-mentioned ingredient and the active material of a particle are kneaded or distributed dissolved using a suitable dispersion medium, and electrode coating liquid is produced. Next, coating is carried out on a charge collector using the obtained coating liquid. As an approach of carrying out coating, methods, such as gravure, gravure reverse, a die coat, and a slide coat, are used. Then, the active material layer of desired thickness is formed through the desiccation process which dries the coating liquid which carried out coating, and it considers as a forward and negative electrode plate.

[0058] As a charge collector used for an electrode plate, metallic foils, such as aluminum and copper, are used preferably, for example. As thickness of a metallic foil, an about 10-30-micrometer thing is used. Moreover, when producing a rechargeable lithium-ion battery using the electrode plate of the positive electrode produced as mentioned above and a negative electrode, the nonaqueous electrolyte which melted the lithium salt of a solute to the organic solvent is used as the electrolytic solution. In this case, as an organic solvent used, there are cyclic ester, chain-like ester, cyclic ether, chain-like ether, etc., there is propylene carbonate etc. as cyclic ester, there is a tetrahydrofuran etc. as cyclic ether, and 1 and 2-dimethoxyethane etc. is mentioned as chain-like ether.

[0059] As lithium salt of the solute which forms nonaqueous electrolyte with the above-mentioned organic solvent, moreover, LiClO_4 , LiBF_4 , LiPF_6 , LiAsF_6 , LiCl , Inorganic lithium salt, such as LiBr , And $\text{LiB 4 LiN (C}_6\text{H}_5\text{) (SO}_2\text{CF}_3\text{)}$ Organic lithium salt, such as 2, $\text{LiC (SO}_2\text{CF}_3\text{)}_3$, $\text{LiOSO}_2\text{CF}_3$, $\text{LiOSO}_2\text{C}_2\text{F}_5$, $\text{LiOSO}_2\text{C}_3\text{F}_7$, $\text{LiOSO}_2\text{C}_4\text{F}_9$, $\text{LiOSO}_2\text{C}_5\text{F}_{11}$, $\text{LiOSO}_2\text{C}_6\text{F}_{13}$, and $\text{LiOSO}_2\text{C}_7\text{F}_{15}$, etc. is used.

[0060]

[Example] Next an example and the example of a comparison are given, and this invention is explained still more concretely.

[0061] The content of an optical-isotropy organization obtains the high softening temperature pitch of 365 degrees C of softening temperatures which are 38 capacity % by adding boron carbide with a mean particle diameter of 14 micrometers 3% of the weight by boron conversion, and heat-treating at 400 degrees C under nitrogen bubbling of the $17\text{Nm}^3/\text{pitch kg}$ by the pressure of 5kg/cm^2 , and G for 5 hours to the reduced pressure pitch of 105 degrees C of example 1 softening temperatures. Cooling solidification of this pitch was extracted and carried out from the reactor. This high softening temperature pitch was ground to the particle with a mean particle diameter of 23 micrometers, and the temperature up was carried out from 130 degrees C to 260 degrees C by part for programming-rate/of 2 degrees C into the air air current, it held for 20 minutes, and oxidation treatment was performed.

[0062] After carrying out the temperature up of this particle to 2800 degrees C to the bottom of an argon ambient atmosphere with the continuation graphitizing furnace among nitrogen-gas-atmosphere mind in 20 hours after carrying out the temperature up and carrying out carbonization processing to 800 degrees C with the programming rate of 50 degrees C/hour in 24 hours and holding it to this temperature for 8 hours, it was made to cool to 100 degrees C in 24 hours, and the boron permutation graphite particle of this invention was obtained. The boron as an element was contained in this graphite particle 2.4% of the weight, and the distance between graphite layers (d_{002}) was the high crystal boron permutation graphite particle whose magnitude (L_a) of the microcrystal of 41nm and the direction of an a-axis the magnitude (L_c) of the microcrystal of 0.335nm and the direction of a c-axis is 77nm. Moreover, it was 0.92 atoms

[in the surface layer element of the boron obtained from the intensity ratio of B1s peak which B1s peak resulting from the permutation dissolution boron near 186eV exists in 1s spectrum of boron measured by XPS, and originates in the boron of B4C near 188eV comparatively detected by XPS] %. Moreover, the rate of the boron combined with the nitrogen near 190eV of 1s spectrum of boron measured by XPS was 3.10 atoms [in the surface layer element detected by XPS] %. Furthermore, when carbon 1S peak of the graphite in carbon 1S spectrum measured by XPS set binding energy of 4f 7 of golden / 2 peak to 84.0eV, the peak existed in 284.1eV. These physical-properties value is collectively described to Table 1 with cell measured value.

[0063] To the reduced pressure pitch of 105 degrees C of example 2 softening temperatures, 2.5 % of the weight was added for boron carbide with a mean particle diameter of 8 micrometers by boron conversion, the same heat treatment as an example 1 was performed, and the high softening temperature pitch which is 357 degrees C of softening temperatures whose content of an optical-isotropy organization is 73 capacity % was obtained. This high softening temperature pitch was ground to the particle with a mean particle diameter of 18 micrometers, and the same oxidation treatment and same carbonization as an example 1 were performed. After carrying out the temperature up to 2400 degrees C to the bottom of an argon ambient atmosphere with the continuation graphitizing furnace after that in 24 hours and holding to this temperature for 9 hours, from that temperature, it was made to cool to 100 degrees C in 36 hours, and the boron permutation graphite particle of this invention was obtained. Many physical properties of this particle are shown in Table 1.

[0064] After heat-treating at 400 degrees C under nitrogen bubbling of the 17Nm3/pitch kg by the pressure of 5kg/cm2, and G for 2 hours to the reduced pressure pitch of 105 degrees C of example 3 softening temperatures, processing temperature was lowered to 350 degrees C, by the same flow rate, bubbling of the air was carried out and it was heat-treated for 1 hour. Consequently, the high softening temperature pitch which is 273 degrees C of softening temperatures whose content of an optical-isotropy organization is 23 capacity % was obtained. Dissolution distribution of boric acid and the natural graphite with a mean particle diameter of 5 micrometers was carried out so that the boron content in the boric acid support natural graphite finally obtained in ethanol on the other hand might become 33% of the weight, ethanol was volatilized by reduced pressure drying after that, and the particle of a natural graphite which carried out homogeneity support of the boric acid was obtained. This particle was mixed at a rate which becomes 5% of the weight as boron to the above-mentioned quantity softening temperature pitch.

[0065] Cooling solidification is carried out after kneading the above-mentioned high softening temperature pitch and the natural graphite which made boric acid support by the kneader. This mixture was ground to the particle with a mean particle diameter of 18 micrometers, and the same oxidation treatment as an example 1 and carbonization processing were performed. Then, the bottom of the argon ambient atmosphere which contained the nitrogen of 10 capacity % with the continuation graphitizing furnace, and after performing a temperature up to 2800 degrees C in 30 hours, held to this temperature for 5 hours, from this temperature to 100 degrees C were made to cool in 24 hours, and the boron permutation graphite particle of this invention was obtained. Many physical properties of this particle are shown in Table 1.

[0066] The same oxidation treatment as an example 1 and carbonization processing were performed below using the particle before oxidation treatment of example 4 example 3. Then, after carrying out the temperature up to 2800 degrees C under the helium ambient atmosphere with the continuation graphitizing furnace in 18 hours and holding to this temperature for 7 hours, from this temperature to 100 degrees C were made to cool in 30 hours, and the boron permutation graphite particle of this invention was obtained. Many physical properties of this particle are shown in Table 1.

[0067] To the carbonaceous ingredient which made even example 5 oxidation treatment be the same as that of an example 1, addition mixing of the natural graphite with a mean particle diameter of 3 micrometers is carried out so that the rate of the natural graphite in the mixture may become 5% of the weight. The boron permutation graphite particle which does not have the welding of a particle in this addition mixture when the same carbonization as an example 1 and graphitization are performed was

obtained. Many physical properties of this particle are shown in Table 1.

[0068] The content of optical anisotropic texture obtains the high softening temperature pitch of 360 degrees C of softening temperatures which are 80 capacity % by heat-treating the reduced pressure pitch of 105 degrees C of example 6 softening temperatures at 400 degrees C under nitrogen bubbling of the 17Nm³/pitch kg by the pressure of 5kg/cm², and G for 5 hours. Cooling solidification of this pitch was extracted and carried out from the reactor. This high softening temperature pitch was ground to the particle with a mean particle diameter of 23 micrometers, and the temperature up was carried out from 130 degrees C to 260 degrees C by part for programming-rate/of 2 degrees C into the air air current, it held for 20 minutes, and non-deliquestce processing was performed.

[0069] The temperature up of this particle was carried out to 800 degrees C with the programming rate of 50 degrees C/hour among nitrogen-gas-atmosphere mind in 24 hours, after carrying out carbonization processing, the Atchison furnace performed graphitization processing and the graphite particle was obtained. To this graphite particle, it adds so that it may become 5% of the weight of the amount of the whole mixture by silicon conversion, and the amorphous silicon whose mean particle diameter is 16 micrometers is put into crucible, and a silicon content carbon material is obtained by heat-treating at 1000 degrees C under nitrogen circulation. The charge and discharge test result of this particle is shown in Table 2.

[0070] To a natural graphite with a mean particle diameter of 16 micrometers which carried out example 7 deashing processing, it adds so that it may become 8% of the weight of the amount of the whole mixture by silicon conversion, and the oxidation silicon whose mean particle diameter is 5 micrometers is put into crucible, and a silicon content carbon material is obtained by heat-treating at 700 degrees C under an air ambient atmosphere. The charge and discharge test result of this particle is shown in Table 2.

[0071] To the boron permutation graphite manufactured in the example 8 example 1, it adds so that it may become 5% of the weight of the amount of the whole mixture by silicon conversion, and single crystal silicon with a mean particle diameter of 14 micrometers is put into crucible, and a silicon content carbon material is obtained by heat-treating at 800 degrees C under nitrogen circulation. The charge and discharge test result of this particle is shown in Table 2.

[0072] Cooling solidification was carried out, after optical anisotropic texture's having done softening melting of the mesophase pitch which is 100% at 290 degrees C of example of comparison 1 softening temperatures and adding 3% of the weight by making boron oxide into boron in it. This pitch that carried out cooling solidification was ground to the particle with a mean particle diameter of 16 micrometers, and the temperature up was carried out from 130 degrees C to 290 degrees C by part for programming-rate/of 2 degrees C into the air air current, it held for 20 minutes, and oxidation treatment was performed. The carbonization / graphitization processing same about this particle as an example 1 was performed, and the carbonaceous particle of the example of a comparison was obtained. Many physical properties of this particle are shown in Table 1.

[0073] Except adding example of comparison 2 boric acid 10% of the weight by boron conversion to a high softening temperature pitch, it is the same approach as an example 3, and the particle with a mean particle diameter of 20 micrometers was prepared. The carbonization / graphitization processing same about this particle as an example 3 was performed, and the carbonaceous particle of the example of a comparison was obtained. Many physical properties of this particle are shown in Table 1.

[0074] Except having made late the cooling rate at the time of example of comparison 3 graphitization, and having made into 120 hours time amount cooled by 100 degrees C, the same processing as an example 1 was performed, and the carbonaceous particle of the example of a comparison was obtained. Many physical properties of this particle are shown in Table 1.

[0075] Except an example of comparison 4 Atchison furnace performing processings for 20 days including the graphitization temperature of 3000 degrees C, and the processing time to cooling, the same processing as an example 1 was performed, and the carbonaceous particle of the example of a comparison was obtained. Many physical properties of this particle are shown in Table 1. According to measurement by XPS of this particle, all the gestalten of the boron which remained had become B-N.

[0076] To the boron permutation graphite manufactured in the example of comparison 5 example 1, it adds so that it may become 5% of the weight of the amount of the whole mixture by silicon conversion, and single crystal silicon with a mean particle diameter of 14 micrometers is put into crucible, and a silicon content carbon material is obtained by heat-treating at 180 degrees C under nitrogen circulation. The charge and discharge test result of this particle is shown in Table 2.

[0077] The boron permutation graphite particle obtained in the evaluation aforementioned example and the example of a comparison as an electrode material, 95 % of the weight and 5% of the weight of each binder of a silicon content carbon material and a carbonaceous particle (polytetrafluoroethylene: 33% of the weight) acetylene black: -- 66 % of the weight and surfactant: -- after kneading 1 % of the weight well and fabricating to a pellet type with a diameter of 13mm, this was put between the nickel network, it was stuck by pressure by the pressure of 3.8 t/cm², the vacuum drying was carried out at 150 degrees C for 5 hours, and the electrode was produced. The lithium foil was used for the counter electrode and the equimolar mixed solvent of the ethylene carbonate and diethylene carbonate which dissolved lithium perchlorate in the concentration of one mol/l. as the electrolytic solution was used. The discharge capacity of a cell was measured under the constant current charge and discharge of current density 0.1 mA/cm². An evaluation result is shown in the following table 1 and Table 2. The boron permutation graphite particle of this invention and a silicon content carbon material have an irreversible capacity smaller than Table 1 and Table 2, and it turns out that it is the thing of high capacity. Moreover, also about a cycle property, property change 10 times after is very as small as about 5%, and a cycle property is [graphite / boron permutation] good.

[0078]

[Table 1]

内容	充電容量 (mAh/g)	放電容量 (mAh/g)	初期 効率 (%)	放電容量 10 回目 (mAh/g)	糊素量 (%)	d002 (nm)	Lc (nm)	La (nm)	XPS 固溶 B ピーク	XPS B4C と しての B (at.%)	XPS BN とし ての B (at.%)	C1sB E (eV)
実施例 1	387	351	90.7	337	2.4	0.335	41	77	あり	0.92	3.10	284.1
実施例 2	391	353	90.3	332	2.1	0.336	37	57	あり	0.38	0.73	284.2
実施例 3	381	344	90.3	330	2.8	0.335	47	82	あり	1.31	1.32	284.1
実施例 4	383	347	90.6	344	2.5	0.335	51	73	あり	1.52	0	284.0
実施例 5	385	349	90.6	331	2.2	0.335	49	90	あり	0.97	1.45	284.1
比較例 1	401	331	82.5	311	2.1	0.337	32	50	あり	1.12	0.93	284.1
比較例 2	420	317	75.5	295	8.6	0.335	48	67	あり	1.71	2.22	284.1
比較例 3	410	321	78.3	299	1.7	0.336	35	61	あり	10.51	1.20	284.2
比較例 4	387	297	76.7	278	0.3	0.338	27	38	なし	0	13.76	284.3

[0079]

[Table 2]

内容	充電容量 (mAh/g)	放電容量 (mAh/g)	初期効率 (%)	添加珪素量 (%)
実施例 6	376	338	90.0	5
実施例 7	485	412	84.9	8
実施例 8	455	403	88.6	5
比較例 5	427	319	74.7	5

[0080]

[Effect of the Invention] As explained above, when the boron permutation graphite of this invention and a silicon content carbon material are used as a negative-electrode ingredient of a rechargeable lithium-ion battery according to this invention, discharge potential is flat, it excels in a cycle property, and the rechargeable lithium-ion battery of high capacity is offered by high density from the conventional carbonaceous ingredient.

[Translation done.]